Developments in Solid State NMR and Potential Applications to Fuel Research*

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The high resolution NMR of two important nuclei (^{13}C and ^{2}D) in the solid state is now a practical possibility. This adds a useful tool to the arsenal of analytical chemistry in the area of solid materials which are insoluble or otherwise not amenable to classical spectroscopic techniques. The study of ^{13}C is made possible by a double resonance method (Proton Enhanced NMR) due to Pines, Gibby and Waugh and has now reached the stage where analysis of some functional groups in coal is possible. A simple physical picture of the method will be given in the talk. As an example, Figure 1 shows spectra on our spectrometer and our computer from a sample of coal from Dr. F. Mayo at SRI working on an ERDA fossil energy related project. At top is the ^{13}C proton enhanced NMR spectrum. At bottom are the computer generated lineshape analyses for four carbon types (aliphatic 26%, ether 13%, aromatic 53% and polycondensed aromatic 8%). In the center is the computer simulation done by adding the four shapes at the bottom and adding some noise--you must agree that there is some similarity with the experimental spectrum. We thus believe the method is quick and reasonably reliable ($\sim$ 10%) for studying whole coals, coal processing, coal by-products and other fuel related materials. We shall show several examples of this in the talk and discuss the advantages and limitations of the method.

The study of ^2D NMR in the solid adds a new possible dimension since isotopic labeling during processing could be followed directly in the solid state. This was considered until recently a particularly nasty nucleus since ^2D linewidth are typically 200 KHz ($\sim$ 1000 ppm wide) in the solid state. A method due to Vega, Shattuck and Pines (Fourier Transform Double Quantum NMR) now brings this nucleus into the realm of high resolution and the possibility of analytical applications. Again, a simple physical picture of the method will be presented in the talk. As an example, Figure 2 shows the first resolution of deuterium chemical shifts in the solid state. At top is an NMR free induction decay taken by the double quantum method. The Fourier transform spectrum at the bottom shows true ^2D chemically shifted lines, one due to the COOD and one due to HDO. Several recent examples of this solid state ^2D spectroscopy will be described and its possibilities and limitations discussed.

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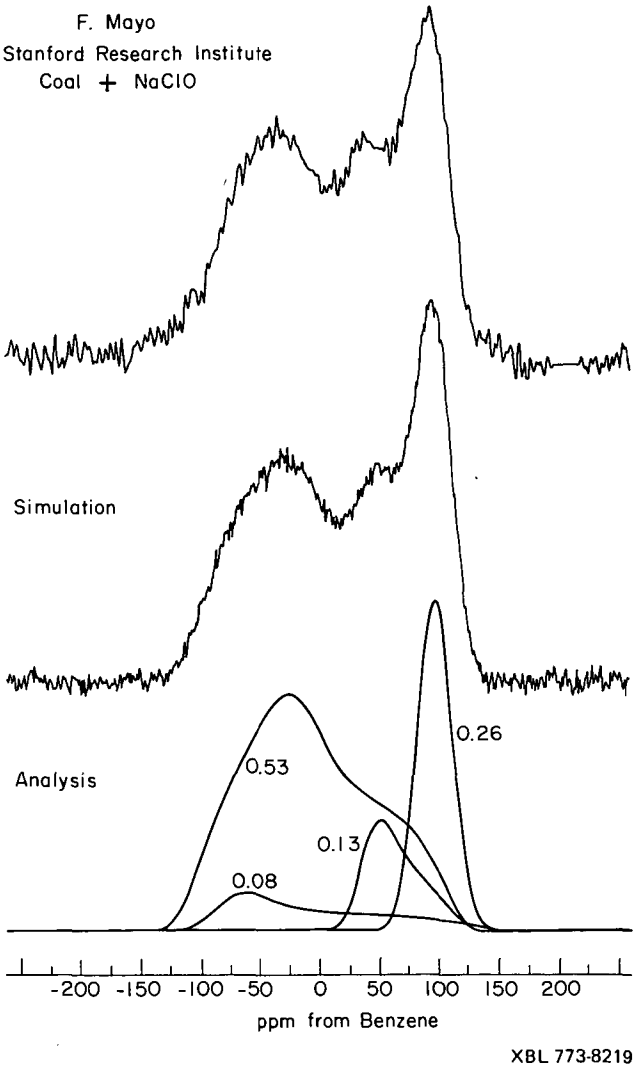
F. Mayo
Stanford Research Institute
Coal + NaClO
Simulation
Analysis
0.53
0.26
0.13
0.08
-200 -150 -100 -50 0 50 100 150 200
ppm from Benzene
XBL 773-8219

Figure 1

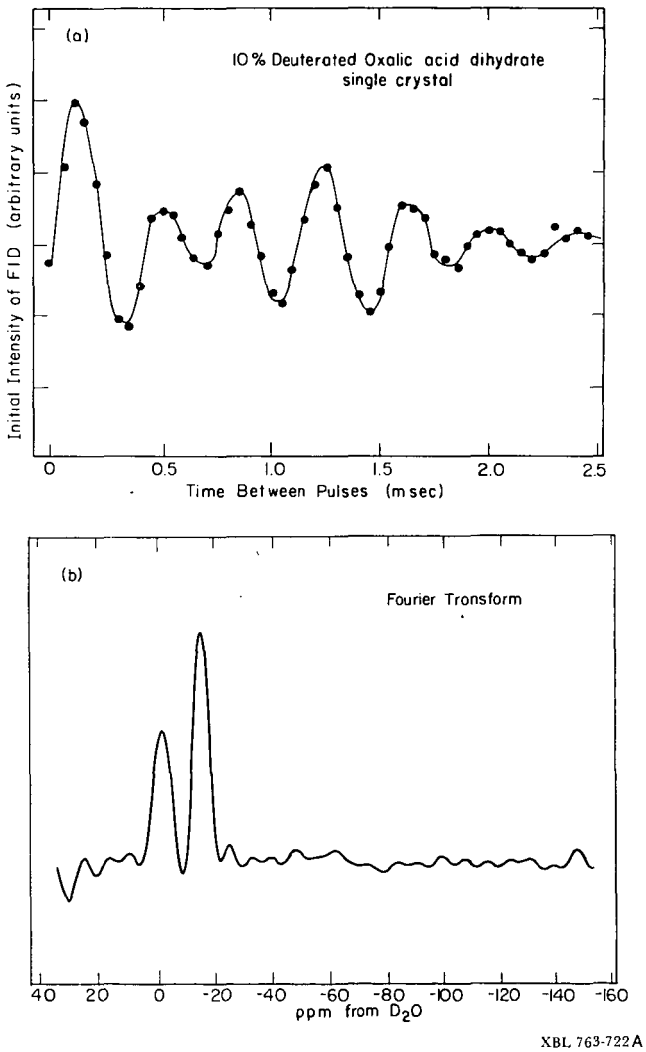
(a)
10% Deuterated Oxalic acid dihydrate
single crystal
Initial Intensity of FID (arbitrary units)
0
0.5
1.0
1.5
2.0
2.5
Time Between Pulses (msec)
(b)
Fourier Transform
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm from D_2O
XBL 763-722A

Figure 2